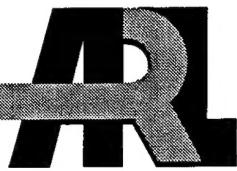


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Corrosion of Aluminum Substrates in Lithium-Ion Batteries

by Wishvender K. Behl and Edward J. Plichta

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Corrosion of Aluminum Substrates in Lithium-Ion Batteries

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Abstract

Controlled potential coulometry was used to investigate the stability of aluminum positive-electrode substrates of rechargeable lithium-ion batteries in solutions of lithium imide salt in ethylene carbonate–propylene carbonate–dimethyl carbonate (EC-PC-DMC) (20:20:60 vol. %). It was found that the protective surface film formed on aluminum in these solutions breaks down at potentials above 3.5 V during the charging of lithium-ion cells, resulting in the corrosion of aluminum substrates and the premature failure of these cells. It was also found that the use of lithium tetrafluoroborate (LiBF_4) as an electrolyte additive prevents the breakdown of the protective film on aluminum substrates, thus preventing their corrosion at potentials above 3.5 V. In contrast to their behavior in the lithium imide solutions, the aluminum substrates were found to be quite stable in lithium methide electrolyte solutions and did not undergo any significant corrosion at potentials up to ~4.5 V compared to the lithium reference electrode.

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1. Introduction

Recently, considerable attention is being given to the choice of a stable, highly conducting, and environmentally friendly electrolyte for rechargeable lithium-ion batteries. Thus, solutions of lithium hexafluoroarsenate (LiAsF_6) in organic solvents used as electrolytes for lithium-ion batteries are increasingly being replaced by solutions of lithium hexafluorophosphate (LiPF_6) because of environmental pollution concerns. However, since LiPF_6 solutions in organic solvents decompose at temperatures above 68 °C, resulting in degradation of the electrolyte, it has been suggested that rechargeable lithium-ion cells should use electrolytes containing solutions of lithium imide salt [1–3], $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (lithium bis(trifluoromethanesulfonyl)imide), in organic solvents. Their high conductivity and thermal stability make such solutions highly suitable as electrolytes for lithium-ion cells (in particular, solutions of lithium imide salt in ternary solvent consisting of mixtures of ethylene carbonate–propylene carbonate–dimethyl carbonate (20:20:60 vol.%)).

It has been found, however, that the aluminum positive-electrode substrates undergo severe corrosion in these solutions at potentials above about 3.5 V during charging operations. On repeated cycling, the aluminum positive-electrode substrates disintegrate, resulting in premature failure of the lithium-ion cells. Therefore, we investigated the corrosion of aluminum in electrolytes containing lithium imide or the newly proposed lithium methide (lithium tris(trifluoromethanesulfonyl)methide) [3–5] salt using the technique of controlled potential coulometry. We also investigated the use of lithium hexafluoroborate as an electrolyte additive for preventing the corrosion of aluminum at high anodic potentials during the charging process. The results are summarized in this report.

2. Experimental Procedures

Three lithium compounds were used as received: lithium imide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, 3M Co.), lithium methide ($\text{LiC}(\text{CF}_3\text{SO}_2)_3$, Covalent Associates, Inc.), and lithium tetrafluoroborate (LiBF_4 , Aldrich Chemical Co.). Three carbonate solvents were dried over molecular sieves before use: ethylene carbonate (EC), propylene carbonate (PC), and dimethyl carbonate (DMC) (all from Grant Chemicals). Lithium foil (Cypress-Foote Mineral Co.) packed over argon and aluminum wire (99.999-percent purity; Johnson Matthey, Alfa Chemicals) were also used as received. We prepared electrolyte solutions by dissolving a requisite amount of lithium imide or lithium methide salt in a ternary mixture of EC-PC-DMC (20:20:60 vol.%) inside an argon-filled dry box (Vacuum Atmosphere Co.).

A three-electrode system was used for all measurements. The reference and counter electrodes were both made from lithium foil pressed onto a nickel screen. The working electrode consisted of a 1-mm-diameter aluminum wire heat-sealed in shrinkable Teflon tubing, so that a 3.6-mm length of the wire was exposed to the solution.

We performed the controlled potential coulometry experiments using an EG&G PAR potentiostat/galvanostat (Model 273). The experiments were computer-controlled by the EG&G PAR Electrochemical Analysis Software (Model 270). All experiments were performed inside the argon-filled dry box, which had a moisture content less than 0.5 ppm.

3. Results and Discussion

Aluminum-metal foils are generally used as substrates for the positive electrode in rechargeable lithium-ion cells such as Li-C/lithium imide in EC-PC-DMC/LiCoO₂. These cells are normally charged to a potential of 4.25 V during charging operations. The aluminum substrates have been found to undergo severe corrosion at the high anodic potentials encountered during the charging process, which results in their disintegration and causes premature failure of the lithium-ion cells.

The aluminum-wire electrodes were found to exhibit an initial potential of about 1.8 V compared to the lithium reference electrode when first introduced in a 1.0 mol solution of lithium imide salt in a ternary mixture of EC-PC-DMC (20:20:60 vol.-%). However, this potential quickly increased to about 2.8 V. It appears that aluminum reacts with the lithium imide electrolyte, resulting in the formation of a thin film on the electrode surface, which causes the initial open-circuit potential to change from 1.8 to ~2.8 V.

The surface film formed on aluminum in these solutions protects the aluminum positive-electrode substrates from corrosion in fresh lithium-ion cells assembled in the discharged state. However, as the lithium-ion cells are charged, the protective film on the aluminum substrates breaks down at the high positive potentials encountered during the charging process, resulting in corrosion and disintegration of the aluminum substrates.

In order to study the corrosion of aluminum substrates in lithium imide solutions, we stepped the potential of the aluminum-wire electrode to more positive values for 300 s, and plotted the current response as a function of time. The aluminum-wire electrode was dipped in 1.0 mol lithium imide solutions in EC-PC-DMC (20:20:60 vol.-%). Figure 1 presents the current-density/time plots at potentials of 3.25, 3.50, 3.75, 4.00, and 4.25 V. We see that at a potential of 3.25 V, the current quickly decreases to a small value, but at higher potentials, the current decreases initially and then begins to increase after ~100 ms. The increase in anodic current at potentials above 3.25 V may be due to the breakdown of the protective surface film on the aluminum electrode, which exposes fresh aluminum and results in its corrosion. The current-density/time plots presented in figure 1 confirm that the aluminum substrates are not stable in lithium imide electrolytes at potentials above ~3.5 V. Choe et al [6] have also recently reported that aluminum is oxidized at potentials below 4 V in polyacrylonitrile-based gel electrolytes containing lithium imide salt.

In order to prevent the corrosion of aluminum substrates at high anodic potentials during the charging of lithium-ion cells, we investigated the use of lithium tetrafluoroborate (LiBF_4) as an electrolyte additive. Figure 2 shows the current-density/time plots obtained from aluminum-wire electrodes in 1.0 mol lithium imide solution in EC-PC-DMC (20:20:60 vol.%) containing 0.2 mol LiBF_4 . We see that in lithium imide solutions containing 0.2 mol LiBF_4 , the surface film on aluminum electrodes was somewhat stabilized and did not break down up to potentials of ~ 4.0 V.

Figure 1. Current-density/time plots obtained at various potentials of aluminum electrode in 1.0 mol lithium imide solution in EC-PC-DMC (20:20:60 vol.%).

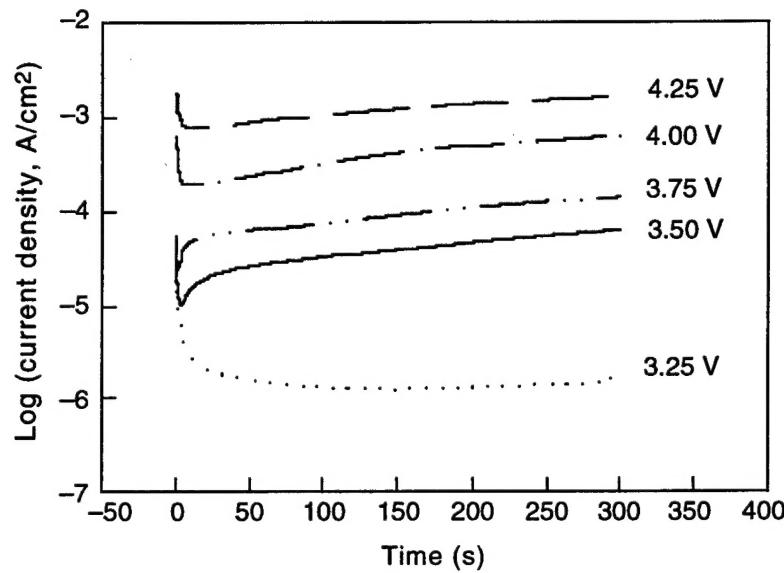
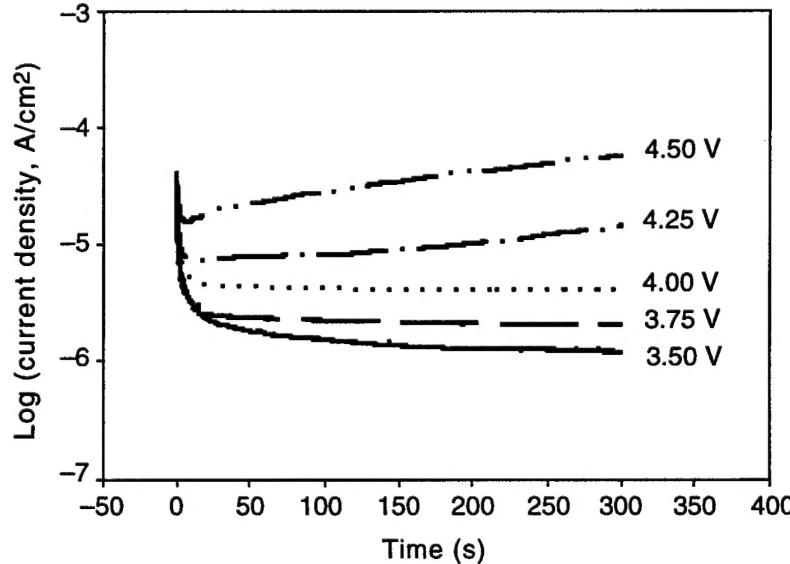


Figure 2. Current-density/time plots obtained at various potentials of aluminum electrode in 1.0 mol lithium imide solution in EC-PC-DMC (20:20:60 vol.%) containing 0.2 mol LiBF_4 .



However, the current-density/time plots at higher potentials were similar to those obtained in lithium imide solutions without the LiBF_4 additive, resulting in a breakdown of the surface film and an increase in the anodic current. In the next series of experiments, we gradually increased the LiBF_4 concentration in lithium imide solutions and recorded the current-density/time plots at each concentration at various potentials. We found that the surface film on aluminum electrodes was completely stabilized in lithium imide solutions containing 0.5 mol LiBF_4 , so that the current decreased asymptotically at all potentials up to 4.5 V, as shown in figure 3.

We also studied the corrosion of aluminum in solutions containing lithium methide salt, which has been recently proposed [3–5] as a stable and highly conducting salt for lithium-ion battery electrolytes. Figure 4 presents the current-density/time plots obtained at aluminum-wire electrodes in 1.0 mol solution of lithium methide in EC-PC-DMC (20:20:60 vol.%). The figure shows that at each applied potential between 3.5 and 4.5 V, the anodic current quickly falls to a steady-state value and, unlike the current in lithium imide solutions, does not show any increase at any potential. This indicates that the aluminum substrates are quite stable in lithium methide electrolyte solutions, and the protective surface film on the substrates would not break down at high anodic potentials during the charging of lithium-ion batteries.

In order to compare the stability of aluminum metal in various electrolyte solutions investigated in this study, we obtained the anodic current of aluminum wire electrodes at $t = 200$ s from the current-time plots presented in figures 1 to 4, and plotted it as a function of the applied potential in figure 5.

Figure 3. Current-density/time plots obtained at various potentials at aluminum electrode in 1.0 mol lithium imide solution in EC-PC-DMC (20:20:60 vol.%) containing 0.5 mol LiBF_4 .

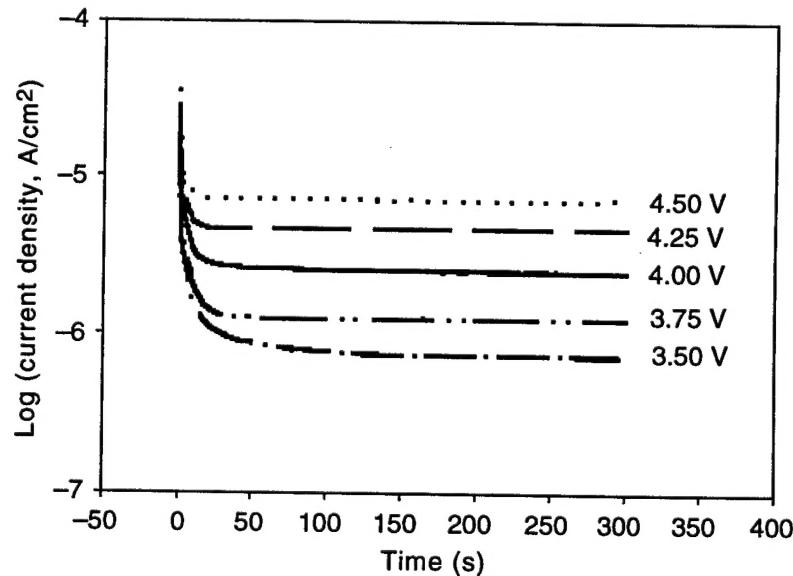


Figure 4. Current-density/time plots obtained at various potentials of aluminum electrode in 1.0 mol lithium methide solution in EC-PC-DMC (20:20:60 vol.%).

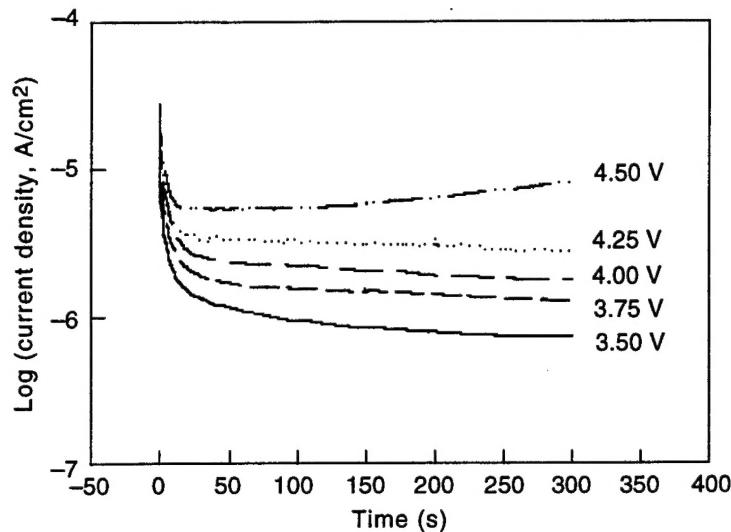


Figure 5. Current densities versus potential plots of aluminum electrode in lithium imide electrolyte, lithium imide electrolyte containing 0.5 mol LiBF_4 , and lithium methide electrolyte. Current densities taken from current-density/time plots presented in figures 1 to 4 at $t = 200$ s.

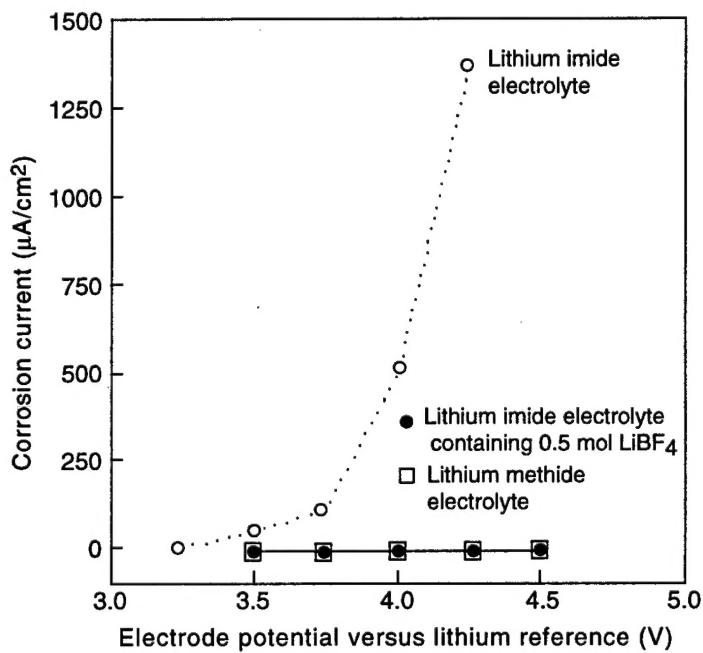


Figure 5 shows that the corrosion currents in lithium imide solutions increase drastically as the electrode potential is increased from 3.25 to 4.5 V, whereas no substantial increase in corrosion currents occurs in the lithium imide electrolyte solution containing 0.5 mol LiBF_4 additive or in the lithium methide solution. The magnitude of the currents at $t = 200$ s in lithium methide solutions was found to be of the same order as the currents in lithium imide solutions containing 0.5 mol LiBF_4 . Thus, the corrosion of aluminum substrates for the positive electrodes in lithium ion cells at high anodic potentials can be prevented by the use of either lithium methide electrolyte or LiBF_4 additive in lithium imide electrolyte.

4. Conclusions

The corrosion of aluminum substrates was studied in newly proposed lithium-ion battery electrolytes containing lithium imide and lithium methide salts. The aluminum metal was found to be quite stable in lithium methide electrolyte solutions, but it was found to undergo corrosion at potentials above ~3.5 V in electrolytes containing lithium imide salt. It was shown that the corrosion of aluminum substrates at high anodic potentials during the charging process in electrolytes containing lithium imide salts can be prevented by the use of LiBF_4 electrolyte additive.

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